

Pyrolysis pretreatment of biomass for entrained-flow gasification

Ruirui Xiao, Xueli Chen, Fuchen Wang, Guangsu Yu *

Key Laboratory of Coal Gasification of Ministry of Education, East China University of Science and Technology, Shanghai 200237, PR China

ARTICLE INFO

Article history:

Received 2 December 2008

Received in revised form 14 June 2009

Accepted 16 June 2009

Available online 12 July 2009

Keywords:

Biomass entrained-flow gasification

Pyrolysis

Semi-char

Tar

Pyrolysis gas

ABSTRACT

The biomass for entrained-flow gasification needs to be pretreated to significantly increase its heating value and to make it more readily transportable. The pyrolysis pretreatment was conducted in a lab scale fixed-bed reactor; the reactor was heated to elevate the temperature at 5 °C/min before holding at the desired pyrolysis temperature for 1.5 h a fixed time. The effects of pyrolysis temperature on the yield, composition and heating value of the gaseous, liquid and solid products were determined. The pyrolysis removed most oxygenated constituents of rice straw while significantly increased its energy density. Meantime, it changes the physical properties of biomass powders. The results show that the angle of repose, the angle of internal friction of semi-char decrease obviously; the bulk density of semi-char is bigger than that of biomass. This could favor the feeding of biomass. Considering yield and heating value of the solid semi-char product and the feeding problem, the best pyrolysis temperature was 400 °C. The results of this study have confirmed the feasibility of employing pyrolyzed biomass for entrained-flow gasification; they are useful for the additional studies that will be necessary for designing an efficient biomass entrained-flow gasification system.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Biomass is the most reliable source of renewable energy; bio-energy will become a major energy resource to cope with global warming and exhaustion of fossil fuel resources [1–4]. Biomass provides cleaner synthetic fuels than coal, shale or tar sands; about 14% of the world's energy is derived from biomass in various forms. It has an important role in both global and national energy planning [5]. Thermo chemical processes are most commonly employed for converting biomass into higher heating value fuels [6].

Biomass gasification is one of the well developed and widely applied technologies for efficient utilization of bio-energy. Entrained-flow gasification of biomass is an attractive technology due to its high gasification efficiency and carbon conversion rate, good quality of gas and relatively low emission of contaminants [7]. Gasification of raw biomass has several disadvantages, such as the low heating value of the pyrolysis gas (5 MJ/Nm³), the high tar content of synthesis gas, difficulty to maintain the stable and continuous feeding, especially in a co-current fed entrained-flow gasifier.

In a typical thermo chemical process for efficient utilization of bio-energy, pyrolysis is the necessary step before gasification of biomass [8]. The products of biomass pyrolysis are gases (primarily CO, H₂, CH₄, C_nH_m, and CO₂), tar and semi-char [9–12]; the relative amounts of gaseous, liquid (tar) and solid (semi-char) products is

dependent on the operating conditions, such as biomass type, temperature, residence time, heating rate, among which pyrolysis temperature is the most significant [13–16]. Pyrolysis of biomass provides a solution to the problems concerned with entrained-flow gasification related to feeding.

Torrefaction is another thermal treatment of biomass at 200–300 °C in absence of oxygen [17]. It is necessary to remove oxygen of biomass before gasification due to the high oxygen content of biomass. But the temperature range of torrefaction is low and the removal of oxygen is limited. The temperature range of pyrolysis is large. During pyrolysis most of the oxygen of biomass is removed resulting in the semi-char solid of higher energy density. The liquid and gaseous products can also be used effectively. The pyrolyzed solid product may be transported directly or mixed with the liquid product to form a slurry for feeding the gasifier. The slurry feeding is ideal and unique for feeding the entrained-flow gasifier.

There are few literature reports of biomass pyrolysis as pretreatment for entrained-flow gasification. In this research, the semi-char, tar and gases products of the lab scale pyrolysis experiments were characterized to illustrate the effect of pyrolysis temperature on composition and yield of biomass pyrolysis in a typical fixed-bed reactor. The results are utilized to confirm the feasibility of pyrolysis pretreatment of biomass for entrained-flow gasification; they are also useful information for additional studies that may be necessary for design of a cost effective and environmental friendly biomass gasification system.

* Corresponding author. Tel./fax: +86 21 64252974.

E-mail address: gsyu@ecust.edu.cn (G. Yu).

2. Experimental

2.1. Material

Rice as the main source of carbohydrate for most Asians and is grown in all Chinese provinces. So rice straw was selected as the biomass of this study. The raw rice straw was obtained from Bao-shan district of Shanghai. It was shredded to 40–80 mesh, dried at 105 °C for 3 h in the oven and then stored in a desiccator. Table 1 presents the proximate analysis and ultimate analysis data (the average of three measurements) of the prepared dry rice straw. The reproducibility of the test procedure is good. The accuracy of the measurements was 0.5%, and the standard deviation of all measurements was <1.7%.

2.2. Experiment flow chart

The schematic flow diagram of the experimental apparatus is shown in Fig. 1. The lab scale pyrolysis system included five sections for heating, reaction, condensation, drying and monitoring. The reaction section is a cylindrical atmospheric pressure stainless steel reactor; the heating section is a furnace and the power source for heating the reactor, gas-feed inlets, and accessories for collecting liquid and gas sample. The small electric tube furnace (50 mm diameter and 70 mm tall) was employed to heat the smaller (50 mm dia) basket reactor to minimize the axial and radial temperature difference. The average temperature difference of 10 sets of the furnace and the in-bed thermocouple readings was 1.57 °C; therefore, the pyrolysis experiments were not limited by the heat transfer of the heating section.

A tailor-made basket containing 60 g of the prepared straw was first placed in the constant temperature zone of the reactor; and nitrogen was circulated through the entire system during 30 min to purge the air of the system. The oven was switched onto heat the reactor to the pre-set pyrolysis temperature between 300 and 700 °C. There were two thermocouples in the furnace: one for the furnace temperature and the other for the actual pyrolysis temperature. The volatile compounds generated during pyrolysis flowed through four cooled condensers, a filter, two CaCl₂ dryer successively. The condensing section consisted of four washing bottles in an ice bath; bottle a was empty to receive most of condensed tar. Bottles b, c, and d were partially filled with methylene chloride to collect the residual tar in the pyrolysis gas. The non-condensable light gas flowed through the surgical cotton packed filter for removing ash and tar. Finally, the gas was dried by CaCl₂ dryer to remove the moisture content of the gas. The gas fraction composition, mainly hydrogen, carbon monoxide, methane, and carbon dioxide, were analyzed using a gas chromatography; the total volume of the light-gas fraction was measured by a gas meter. The solid residue remaining in the basket and the liquid fraction were weighed after the system cooled down.

2.3. Experimental conditions and test methods

Before each test run began, the reactor was purged with nitrogen for 30 min at 0.35 L/min to drive off the air. The raw straw

filled basket was then heated at a rate to elevate 5 °C/min to 200–700 °C at 0.1 MPa and kept for 1.5 h at final temperature till there was no pyrolysis gas.

The amounts of C, H, O, N, and S in the pyrolysis products were analyzed quantitatively by Vario MACRO Elemental Analyzer of Elementar, Germany. The frame character of semi-char was studied using JSM-6360LV Scanning Electron Micrograph of JEOL.

The pore surface area (S_{BET}), pore volumes and average pore diameter measurements were carried out using a modified Micromeritics ASAP-2020 automated surface area analyzer. Samples were outgassed at 105 °C overnight under vacuum to a final pressure of 0.25 Pa. For all samples, N₂ adsorption isotherms at 77 K were measured for the relative pressure (P/P_0) ranging from 0.01 to 0.995.

The angle of internal friction was measured using SDJ-I equal strain direct shear apparatus of Nanjing Ningxi Soil Instrument.

Gas component (CO, CH₄, CO₂, and H₂) was quantified using GC-9790 Chromatography with a thermal conductivity detector and a double injector connected to two columns. The carrier gas was high purity nitrogen. The padding was GDX.

The tar composition was investigated with Clarus 600 GC/MS analysis instrument of PerkinElmer, America.

3. Experimental results and discussions

3.1. Mass yield of pyrolysis products

3.1.1. Definition of mass yield

The mass yield is defined as the mass of pyrolysis products to that of the prepared biomass charged to the basket reactor. Thus on the dry basis (d): $\eta_i = \frac{M_i}{M_{\text{biomass}}}$.

In which, η_i is the mass yield of pyrolysis products, M_i the mass of all pyrolysis products (dry semi-char, tar, and gases), and M_{biomass} is the mass of the dry prepared biomass charged.

3.1.2. Effect of pyrolysis temperature on mass yield of pyrolysis products

The effect of pyrolysis temperature on mass yield of pyrolysis products is significant. The distribution of the fractions presents different trends as shown in Fig. 2.

The mass yield was obtained by means of the mass balance. For each set of parameters, three runs were carried out under the identical conditions to check the reproducibility of the experiments. The data showed good reproducibility with the standard deviation of <3%.

The increasing pyrolysis temperature resulted in declining yield of semi-char and increasing yield of the gases due to semi-char decomposition releasing volatile matters at the higher temperature. The reduction in the char yield at a higher temperature is consistent with the increase in the volatile matter. The liquid fraction yield reached a maximum at about 500 °C. However, the tar decomposed at a higher temperatures resulting in a lower liquid yield with a concurrent higher gas yield. At a low pyrolysis temperature, the gas release was slow; the main reaction was carbonization. The rising pyrolysis temperature substantially increased gas release resulting in more tar condensate until the point of maximum tar yield. At an even higher pyrolysis temperature, tar

Table 1
Proximate and ultimate analysis of the rice straw.

Proximate analysis (%) ^a			Ultimate analysis (%) ^a					HHV (MJ kg ⁻¹)
V	FC	A	C	H	N	O ^b	S	17.10
71.70	18.58	9.72	43.68	5.70	0.97	39.72	0.21	

^a Weight percentage on dry basis.

^b By difference method.

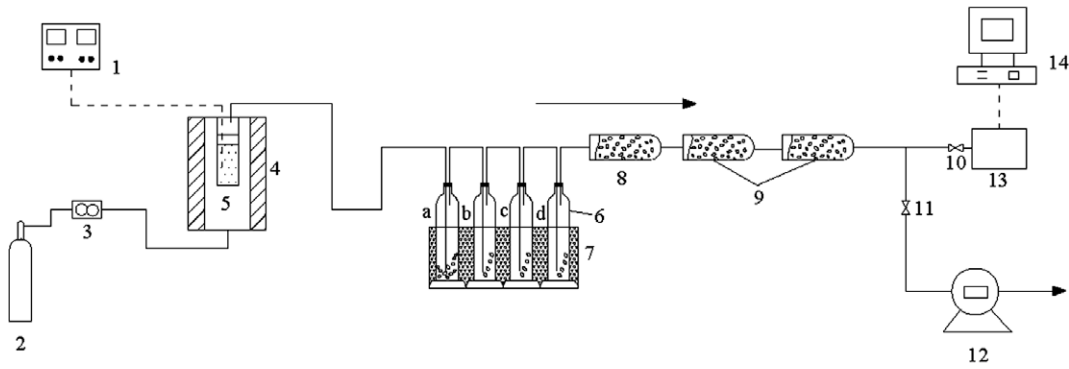


Fig. 1. Schematic flow diagram of the lab scale pyrolysis system. (1) Temperature controller, (2) N₂ cylinder, (3) flow meter, (4) electric furnace, (5) pyrolysis reactor, (6) washing bottles, (7) condenser, (8) filter, (9) dryer, (10 and 11) valves, (12) gas meter, (13) GC, and (14) computer.

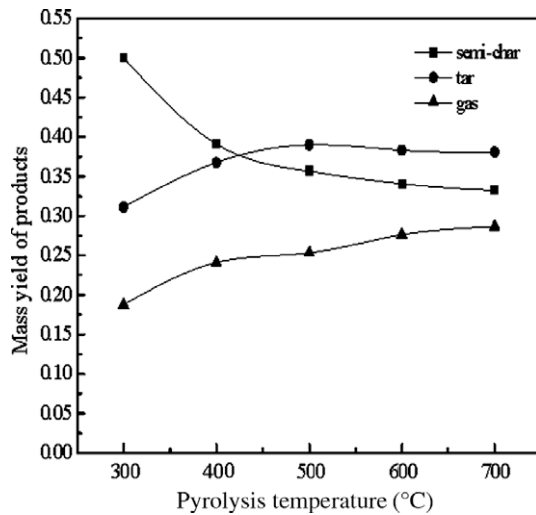


Fig. 2. Effect of pyrolysis temperature on mass yield of the products.

was partially decomposed to form non-condensable gases [18] which contributed to the observed higher gas yield.

3.2. Analysis of semi-char

3.2.1. Definition of energy yield and Φ

The energy yield is defined as follow:

$$\eta_E = \eta_{\text{semi-char}} \left(\frac{\text{HHV}_{\text{semi-char}}}{\text{HHV}_{\text{biomass}}} \right)_d$$

In which, η_E is the energy yield of semi-char, $\eta_{\text{semi-char}}$ the mass yield of semi-char, $\text{HHV}_{\text{semi-char}}$ the heating value of dry semi-char, and $\text{HHV}_{\text{biomass}}$ is the heating value of the dry prepared biomass charged.

ϕ is defined as the oxygen removal degree during biomass pyrolysis.

Thus on the dry basis (d):

$$\phi = \frac{O_{\text{biomass}} - O_{\text{semi-char}} \times \eta_{\text{semi-char}}}{O_{\text{biomass}}}$$

In which, O_{biomass} , $O_{\text{semi-char}}$ are the oxygen content of the dry prepared biomass charged and semi-char.

3.2.2. SEM of semi-char

Figs. 3–6 present SEM photomicrographs of semi-char samples obtained in the test runs of different pyrolysis temperatures. The

semi-char product was porous with many micropores, mesopores and macropores of irregular shape and different size. The pore size of the 300 °C semi-char was more uniform than the 400 °C semi-char because biomass composed tempestuously at 400 °C. There were many globular materials on the surface of the 600 °C semi-char. Furthermore, the fracture surface of the 600 °C semi-char is more smooth than that of the 500 °C sample. Such phenomena indicate that the surface of the 600 °C semi-char partially melted at the high temperature and that cellulose, hemicellulose and lignin of the biomass were destroyed. The breakdown of carbon framework led to the tenacity loss and a lower hardness [19]. Considering the semi-char yield and its physical properties, the best pyrolysis temperature was 400 °C.

3.2.3. Specific surface of semi-char

The characteristics (BET surface area, pore volume and pore diameter) of semi-char are listed in Table 2. The accuracy of the measurements is 3%. The tests were carried out in duplicate. The data show good reproducibility of the test runs and the coefficient of variation of each test of <2%.

Table 2 shows that the BET specific surface area and pore volume of the semi-char increased with the pyrolysis temperature with the greatest increase took place at 500–600 °C. Such porous structure suggests semi-char had respectable adsorptive capacities for many gaseous and liquid constituents of the product. Pore diameter was 41.26 nm at a pyrolysis temperature of 300 °C, it reached the maximum of 82.30 nm at about 500 °C. The shrinkage of the char and realignment of its structure led to the observed

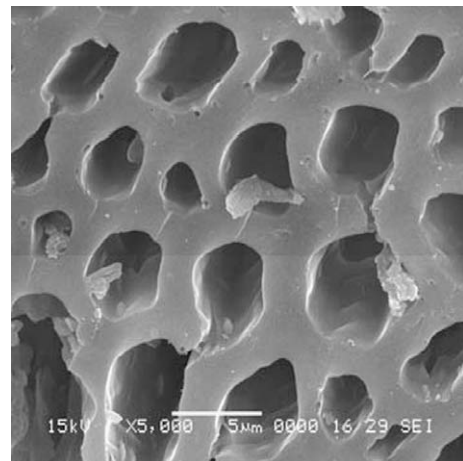


Fig. 3. SEM of the 300 °C semi-char.

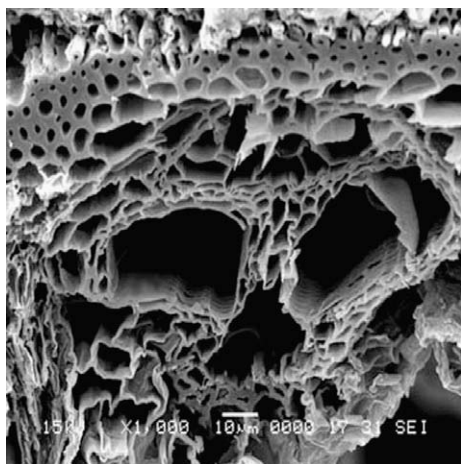


Fig. 4. SEM of the 400 °C semi-char.

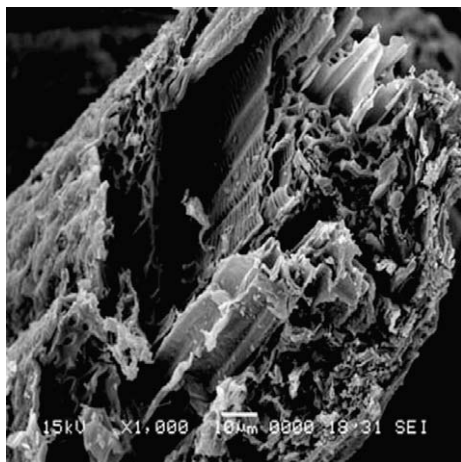


Fig. 5. SEM of the 500 °C semi-char.

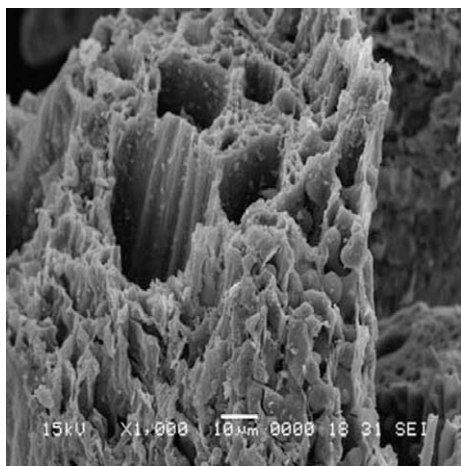


Fig. 6. SEM of the 600 °C semi-char.

3.2.4. Ultimate analysis and energy yield of semi-char

Data of the ultimate analysis and HHV of semi-char at different pyrolysis temperatures are listed in Table 3. The accuracy of equipment and repeatability of measurements have been described in Section 2.1. The semi-char carbon content was higher while its oxygen content was lower than those of the prepared biomass (Table 1). The carbon content increased while its oxygen content decreased with the increase in pyrolysis temperature. At higher temperatures, the functional groups of biomass ruptured and/or recombined to form volatile matters resulting in the observed changes of the elemental composition. Pyrolysis is a process of removing volatiles of biomass; most of the carbon remains in semi-char while most of the oxygen is gone with the volatiles. The low oxygen semi-char is the ideal feed for entrained-flow gasification of biomass.

The pyrolysis increased the higher heating value (HHV) of biomass significantly; HHV of the semi-char was about 36% higher than that of the biomass. At a higher temperature, biomass was more pyrolyzed with nearly complete oxygen removal resulting in the higher HHV semi-char. The heating value of biosyngas produced from the entrained-flow biomass gasification system will be higher with the higher HHV semi-char feed.

Fig. 7 presents Φ value and oxygen/carbon ratio of semi-char samples obtained in the test runs of different pyrolysis temperatures. The Φ value increased while oxygen/carbon ratio decreased with the increase in pyrolysis temperature. The semi-char oxygen content is low when ϕ is high. So the oxygen removal degree increased with the temperature improved. HHV of semi-char was lower with the higher oxygen/carbon ratio except for individual case.

The energy yield of semi-char at different pyrolysis temperatures is presented in Fig. 8. The energy yield decreased with the increase in pyrolysis temperature and the extent of decline was lightened distinctly at higher temperature. Because at high pyrolysis temperatures, volatile matters were removed to exist in liquid and gaseous forms so part of the energy was transferred to liquid and gas.

Considering the mass yield and energy yield of semi-char, 400 °C was regarded as the optimal pyrolysis temperature for biomass pretreatment for entrained-flow gasification.

3.2.5. Influence of slow pyrolysis on transportation characteristics of biomass powders

Angle of repose, bulk density and angle of internal friction are important property of power, which are important parameters to characterize flow characteristics of power. The smaller the angle of repose, the better the flow characteristics of material. The tests were carried out in duplicate and the reproducibility was good.

Angle of repose, bulk density and angle of internal friction of biomass and semi-char are listed in Table 4. The angle of internal friction of semi-char decreases with the increase of temperature. The heat energy destroyed the intermolecular bond and the bond action provided by the mechanical interlocking when the temperature was increased. The shape of particles was close to sphere after pyrolysis and the adhesion between particles weakened. So the angle of internal friction of semi-char decreased, which favoured the transportation of biomass entrained-flow gasification.

The angle of repose of semi-char decreased obviously and the bulk density of semi-char was larger than that of biomass. It can be seen in Table 4 that the angle of repose is the smallest and the bulk density is the largest for 400 °C semi-char. So 400 °C semi-char is the best for transportation compared with others.

Angle of repose, bulk density and angle of internal friction of biomass were all improved through pyrolysis, which is beneficial to transportation. So the transportation and feed of biomass entrained-flow gasification can be continuous and controlled.

reduction of the average pore size the semi-char 600 °C relative to that of 500 °C. The lower average pore diameter of the semi-char 600 °C is consistent with its much higher surface area and pore volume and the SEM results.

Table 2

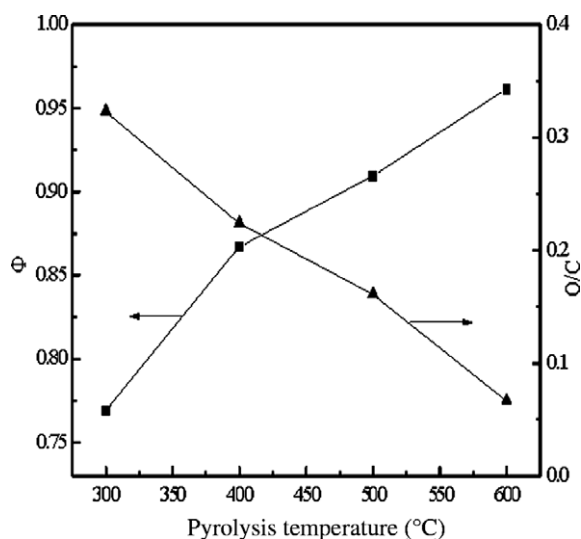
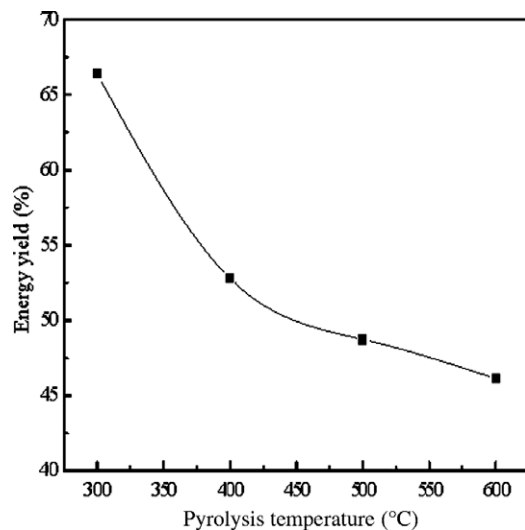
Effect of pyrolysis temperature on specific surface area, pore volume and average pore size.

Temperature (°C)	BET surface area (m ² g ⁻¹)	Volume (×10 ⁻³ cm ³ g ⁻¹)	Average pore size (nm)
300	4.15	1.02	41.26
400	5.22	1.12	54.56
500	16.60	3.91	82.30
600	53.59	1365.84	59.68

Table 3

Effect of pyrolysis temperature on ultimate analysis and HHV of the semi-char product.

Temperature (°C)	Mass yield (%)	HHV (MJ/kg)	Ultimate analysis (%) ^a				
			C _d	H _d	S _d	N _d	O _d
300	50.10	22.72	56.83	4.31	0.27	1.10	18.37
400	39.14	23.16	60.38	3.14	0.29	1.07	13.54
500	35.67	23.15	62.15	2.43	0.32	1.06	10.01
600	34.07	23.20	67.7	1.69	0.29	1.09	4.52

^a Weight percentage on dry basis.**Fig. 7.** Effect of pyrolysis temperature on O/C and Φ of semi-char.**Fig. 8.** Effect of pyrolysis temperature on energy yield of semi-char.

3.3. Analysis of pyrolysis tar

3.3.1. Characteristics of tar

The pyrolysis liquid product is brownish tar with a strong irritating odor. The tar is a mixture of polar organics and water. Table 5 presents the characteristics of tar produced by biomass pyrolysis conducted at 300–700 °C. The reproducibility of the duplicated test runs was good with a coefficient of variation of the tests <1.5%.

The elemental composition of pyrolysis tar was dependent on the pyrolysis conditions. The high water and oxygen contents were responsible for its medium heating value. The higher oxygen content of the tar at the higher temperature might have been the result of more complete oxygen removal during pyrolysis. The high oxygen content is indicative of the presence of many highly polar organic compounds of high viscosities and relatively low stability. Pyrolysis can remove most of the oxygen of biomass in form of volatile matters. Some of the volatiles condensed to form tar below 300 °C. The carbon content, oxygen content and heating value were highest at 500 °C, which resulted from the most condensate in the volatiles and highest tar yield (see in Section 3.1.2) at this pyrolysis temperature. The tar may be employed to mix with semi-char in a given ratio to make the desired slurry for feeding the entrained-flow biomass gasification system.

3.3.2. GC/MS results of tar

GC/MS analyses were conducted at different temperatures with the resulting chemical compositions shown in Table 6. The reproducibility of the duplicated test run was good with the standard deviation of each product <5%.

Some complex compounds identified in tar were organic compounds such as hydrocarbon, phenol, acid, ketone, ester, and so on. The content of these compounds was more than 60%. The acid reduced between 300 and 700 °C because some of the volatile recombined under higher temperature to reduce the condensate content. The acid and alcohol content reduced significantly and the ester content increased between 300 and 400 °C on account of the increasing reaction chances of alcohol and acid to form esters at higher temperatures. The main reason of the decrease of heterocycles such as furan and pyran category with increasing temperature was that the heterocycles fracture and recombine at high temperature. The internal structure of biomass fractured fully to form short-chain aliphatic compounds at higher temperature, which led to the decrease of aromatic compounds and the increase of aliphatic compounds. The water content was the highest at 500 °C because hydroxyl of semi-char cracked rapidly to dehydrate

Table 4

Angle of repose, bulk density, and angle of internal friction of biomass and semi-char.

	Angle of repose (°)	Bulk density (kg m ³)	Angle of internal friction (°)
Straw	51.1	150.1	36.0
300 °C semi-char	43.2	197.2	35.7
400 °C semi-char	39.6	263.3	32.9
500 °C semi-char	44.9	214.5	30.6
600 °C semi-char	42.9	235.6	30.1

Table 5

Effect of pyrolysis temperature on moisture content, elemental composition and heating value of the tar product (wt.% as received).

Temperature (°C)	Physical characteristic (%)						Heating value (on dry basis) (MJ kg)
	Moisture content	C	H	N	S	O	
300	31.40	19.01	5.85	0.31	0.07	43.36	17.25
400	30.47	19.10	5.90	0.38	0.10	44.05	17.39
500	26.62	20.65	6.91	0.35	0.09	45.38	18.02
600	28.36	19.39	6.32	0.39	0.12	45.42	17.53

Table 6

Effect of pyrolysis temperature on chemical composition of the tar product.

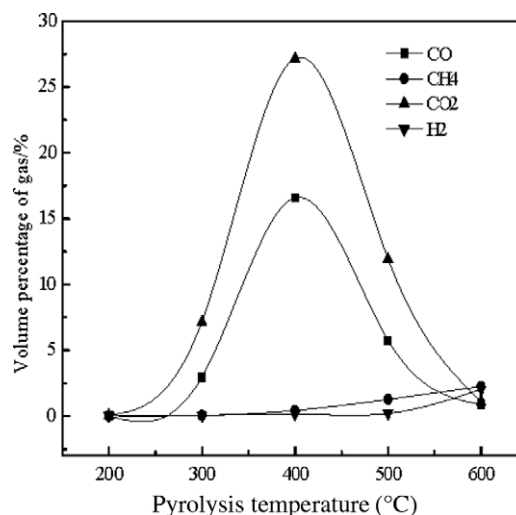
Materials (%)	Pyrolysis temperature (°C)				
	300	400	500	600	700
Moisture	18.10	15.20	33.31	21.00	31.83
Acid	36.24	29.70	30.80	30.47	30.72
Phenol	3.76	4.08	4.61	9.99	8.43
Ketone	8.49	7.01	17.01	6.39	4.61
Alcohol	5.69	6.40	4.77	4.86	5.92
Aldehyde	6.14	–	–	–	–
Ester	–	7.30	3.05	7.83	8.96
Furan	–	1.70	1.83	1.80	3.60
Others	21.58	28.61	4.62	17.66	5.93

at this temperature. Similar results were reported by other authors for this kind of residue [20–22]. To use the tar, the slurry feeding mode mentioned above for biomass entrained-flow gasification is a good idea.

3.4. Effect of temperature on gas products

The effect of pyrolysis temperature on the gaseous products is shown in Fig. 9. The gases, mostly H₂, CO, CH₄, and CO₂, were measured by gas chromatography. The lower heating value of the pyrolysis gases, 5485–10,109 kJ/Nm³, may be utilized for heating when they are fed to the gasification system to obtain a higher recovery of energy from the biomass.

The distribution of the straw pyrolysis products depends on the thermal decomposition of the majority components (cellulose, hemicellulose and lignin). Most of the thermal cracking products of cellulose and lignin are volatile matters and coke, respectively. Shafizadeh reported that hemicellulose, as represented by xylan, decomposed in the range between 220 and 320 °C, cellulose at 250–360 °C, and lignin underwent gradual decomposition at 180–500 °C. The loss of cellulose was relatively low at <240 °C. It depolymerized to form carbonyl and carboxyl mostly [23,24]. The non-condensable gases came from rupture of some functional groups. Hydrogen was produced by cracking of volatiles. CH₄ resulted from cracking and depolymerization reactions while CO and CO₂ were produced from decarboxylation and depolymerization or secondary oxidation of carbon. These reactions were favored with increasing temperature, which led to greater gas production. Productions of CO and CO₂ went through a maximum at about 400 °C due to degradation of hemicellulose and cellulose [25]. The formation of CH₄ and other light hydrocarbons were related to the degradation of lignin.

**Fig. 9.** Effect of pyrolysis temperature on composition of the gaseous products.

Large quantities of tar, water, CO, and CO₂ resulted from the rupture of C–C and C–O bonds between 240 °C and 400 °C. CO₂ was formed by the rupture of the glucosidic linkage and C–O bonds in the pyran ring, while CO and water from keto and primary alcohol groups. Above 400 °C, biomass aromaticity increased and formed graphite structure gradually with the result of less production of CO and CO₂. As the temperature was increased, some C₂ and C₃ hydrocarbons dehydrogenated to form massive low-molecular gases such as H₂ and CH₄. The evolution of CO and CO₂ at higher temperatures was due to lignin, possibly through the release of COOH groups and rupture of C–O groups, producing water at the same time. The formation of methane was due to the release of methoxy groups, involving the rupture of C–C bonds, and it was controlled by hydrogen transfer reaction. The best pyrolysis temperature of the experimental system was 400 °C for most effective oxygen removal and bio-energy recovery.

4. Conclusions

The pyrolysis temperature had significant effects on composition, structure, heat value of the gaseous, tar liquid, and semi-char solid products. The pyrolysis removed most oxygenated constituents of rice straw while significantly increased its energy density. The angle of repose, the angle of internal friction of semi-char de-

crease obviously; the bulk density of semi-char is larger than that of biomass. This could favor the feed of biomass. Considering yield, heating value and transportation characteristics of the solid semi-char product, the best pyrolysis temperature was 400 °C. The results of this study have confirmed the feasibility of employing pyrolyzed biomass for entrained-flow gasification; they are useful for the additional studies that will be necessary for designing an efficient biomass entrained-flow gasification system.

Acknowledgements

This study was supported by the National Basic Research Program of China (No. 2004CB217703), and Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT-IRT0620).

References

- [1] Dowaki Kiyoshi, Mori Shunsuke. Biomass energy used in a sawmill. *Appl Energy* 2005;80:327–39.
- [2] Savolainen Kati. Co-firing of biomass in coal-fired utility boilers. *Appl Energy* 2003;74:369–81.
- [3] L  De Jacques. Solar thermochemical conversion of biomass. *Solar Energy* 1999;65(1):3–13.
- [4] Fujino Junichi, Yamaji Kenji, Yamamoto Hiromi. Biomass-balance table for evaluating bioenergy resources. *Appl Energy* 1999;63:75–89.
- [5] Senoz Sevgi. Slow pyrolysis of wood barks from *Pinus brutia* Ten and product compositions. *Bioresource Technol* 2003;89:307–11.
- [6] Ozbay Nurg  l, P  t  n Ays  e, P  t  n Ersan. Structural analysis of bio-oils from pyrolysis and steam pyrolysis of cottonseed cake. *J Anal Appl Pyrol* 2001;60:89–101.
- [7] Keyun Deng. Development strategy of China's bioenergy in 21st century. *Electr Power* 2000;33(9):82–4.
- [8] Wen Lihua, Wang Shurong, Luo Zhongyang, et al. Multicomponent kinetic model of biomass pyrolysis. *J Zhejiang Univ (Eng Sci)* 2004;39(2):247–52.
- [9] Ma Chengrong, Xiao Bo, Yang Jiakuan. Study on the effects of operating conditions of biomass pyrolysis. *Environ Biol Technol* 2005;5:10–2.
- [10] Chen Yi, Luo Yonghao, Lu Fang. The progress in biomass pyrolysis mechanism research. *Indus Heat* 2006;35(5):4–7.
- [11] Yanhua Lai, Mingxin Lv, Chunyuan Ma, et al. Study on the characteristics and dynamics of pyrolysis process agricultural residues. *Acta Energeiae Solaris Sin* 2002;23(2):203–6.
- [12] Demirbas A, Arin G. An overview of biomass pyrolysis. *Energy Sour* 2002;24(5):471–82.
- [13] Demirbas A. Gaseous products from biomass by pyrolysis and gasification: effects of catalyst on hydrogen yield. *Energy Convers Manage* 2002;43(7):897–909.
- [14] Demirbas A. Biomass resource facilities and biomass conversion processing for fuels and chemicals. *Energy Convers Manage* 2001;42(11):1357–78.
- [15] Di Blasi C, Signorelli G, Di Russo C, et al. Product distribution from pyrolysis of wood and agricultural residuals. *Indus Eng Chem Res* 1999;38:2216–24.
- [16] Minkova V, Marinov SP, Zanzi R, et al. Thermochemical treatment of biomass in a flow of steam or in a mixture of steam and carbon dioxide. *Fuel Process Technol* 2000;62:45–52.
- [17] Bergman PCA, Prins MJ. Torrefaction for entrained-flow gasification of biomass. ECN-C-05-067.
- [18] Hong Tan, Shurong Wang, Zhongyang Luo, et al. Pyrolysis behavior of cellulose, xylan and lignin. *J Fuel Chem Technol* 2006;34(1):61–5.
- [19] Weiwei Zhang, Xueli Chen, Guoyong Zeng, et al. Influence of slow pyrolysis on physical properties of biomass powers. *Chem Eng (China)* 2008;36(3):60–3.
- [20] Zhang Quanguo, Xu Guoqiang, Yang Qunfa, et al. Experimental study of the thermophysical characteristics of biomass tar. *J Huazhong Agric Univ* 2001;20(5):493–6.
- [21] Zhang Suping, Yan Yongjie, Ren Zhengwei, et al. Analysis of liquid product obtained by the fast pyrolysis of biomass. *J East China Univ Sci Technol* 2001;27(6):666–8.
- [22] Li Jihong, Lei Tingzhou, Song Huamin, et al. Analysis of chemical component of biomass-based tar by GC/MS. *Henan Sci* 2005;23(1):41–3.
- [23] Shafizadeh F. In: Anderson LL, Tillman DA, editors. *Fuels from waste*. New York: Academic Press; 1977.
- [24] Nunn TR, Howard JB, Longwell JP, et al. Product compositions and kinetics in the rapid pyrolysis of sweet gum hardwood. *Indus Eng Chem Process* 1985;24(3):836–44.
- [25] Gonz  lez Juan F, Ramiro Antonio, Gonz  lez-Garc  a Carmen M. Pyrolysis of almond shells. Energy applications of fractions. *Indus Eng Chem Res* 2005;44:3003–12.